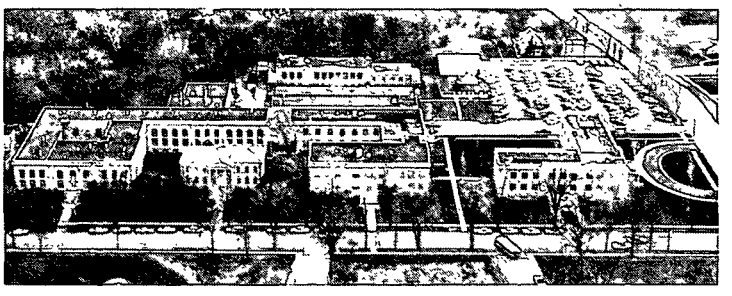

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IDENTIFICATION OF POLYMERS IN PAPER BY PYROLYSIS GAS CHROMATOGRAPHY. REDUCTION OF PAPER INTERFERENCE BY PREPYROLYSIS.

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Identification of Polymers in Paper by Pyrolysis Gas Chromatography. Reduction of Paper Interference by Prepyrolysis

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Identification of polymers in paper by pyrolysis gas chromatography. Reduction of paper interference by prepyrolysis.

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A sequential pyrolysis procedure has been developed to facilitate the identification of polymers in paper by pyrolysis gas chromatography. The sample was subjected to low-temperature pyrolysis (prepyrolysis) at 400°C to char the paper; subsequent pyrolysis at 850°C produced characteristic pyrograms of polymers with minimal interference from the paper substrate. Of twenty-one polymers added to paper, twelve yielded identifiable "fingerprint" pyrograms by employing the prepyrolysis-pyrolysis sequence.

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INTRODUCTION

Pyrolysis gas chromatography (PGC) has been used extensively for the analysis of polymers [1], but its application to the identification of polymers in paper has been rather limited [2-8]. Polymer-containing papers are most often analyzed to determine the additives used in a product, or to identify deposits and contaminants inadvertently picked up during paper manufacturing, especially from recycled fiber [7,8].

Pyrograms of polymer-paper combinations are complex, because they contain peaks representing pyrolysis products of the paper as well as the polymer. As a result, identification of the polymer of interest is often extremely difficult. This is especially true for small amounts of polymer because the pyrolysis products of the paper dominate the pyrogram. Some investigators have pyrolyzed paper without polymer and then have attempted to subtract visually the peaks due to the paper from the pyrogram of the mixture [2,6]. Such an approach is difficult under the best of conditions, and it is likely to fail when there are secondary pyrolysis reactions between the pyrolysis products of the polymer and the paper. Furthermore, a paper identical to that in the polymer-paper combination is not always available.

Whenever possible, the polymer is removed from the paper prior to analysis. Coatings and saturants are extracted with solvents, and deposits and discrete plastic fragments are lifted from the paper surface [7,8]. However, a preliminary separation of polymer and paper is not feasible for all analyses. Crosslinked polymers cannot be extracted, and small polymer specks often cannot be dissolved in solvents or removed without paper contamination. A technique is needed to enhance the response of the polymer in PGC relative to that of the

paper. This has been achieved with styrene-containing polymers [4]. Low-temperature (600°C) prepyrolysis decomposed the paper, and its products were vented; subsequent pyrolysis at 725°C yielded pyrograms used to determine styrene-butadiene.

The current investigation was undertaken to more fully evaluate the prepyrolysis technique for identification of polymers in paper. Sufficient quantities of a large number of polymers were found to survive prepyrolysis to be identified by subsequent pyrolysis at higher temperature. Optimized pyrolysis and gas chromatographic (GC) conditions were developed to permit characterization of the polymers via "fingerprint" pyrograms or mass spectral (MS) analysis of pyrolysis products.

EXPERIMENTAL

PGC and PGC/MS instrumentation and conditions

Pyrolyses were performed with a CDS Pyroprobe 120 (Chemical Data Systems, Oxford, PA, U.S.A.). For prepyrolysis, the sample probe was inserted into a 15-cm x 12-mm Pyrex tube closed at both ends with silicone septa and caps. One septum was bored out to admit the probe. After purging with nitrogen for 1 min, the tube was capped and the sample was prepyrolyzed for 2 min at 400°C. The probe was withdrawn from the tube and inserted into the GC interface mounted on a Hewlett-Packard 5890A GC.

Pyrolysis was performed at 850°C for 10 s with the ramp setting on the pyrolyzer in the "off" position. The GC interface was maintained at 200°C. Products of pyrolysis were separated on a 6-ft. x 2-mm I.D. glass column packed with 1% SP1000 on 60/80-mesh Carbopak B. Column temperature was programmed from

40 to 200°C at 8°C/min, and the helium carrier gas flow rate was 20 ml/min. Injector temperature on the GC was 250°C, and the flame ionization detector temperature was 300°C. Data were recorded on a Hewlett-Packard 3388A integrator.

A Hewlett-Packard 5985B GC/MS was used for identification of pyrolysis products. All conditions were the same as on the 5890A GC, except that a higher carrier gas flow rate, 30 ml/min, was required for proper operation of the jet separator. This reduced retention times by about 1 min. Pyrolysis products were identified by comparing their mass spectra, via computer, with those in the Wiley Library.

Pulps, papers, and polymers

One sample each of bleached hardwood kraft, unbleached softwood kraft, and thermomechanical pulp (TMP) was selected for study. Laboratory-made papers were prepared from the bleached kraft pulp.

Polymers typical of those used in paper saturation, coating, sizing, and as dry- and wet-strength additives were studied (Polymer Sample Kit, Scientific Polymer Products, Ontario, NY, U.S.A). The polymers were pyrolyzed alone and after addition to the paper as a solution or a melt. Samples for pyrolysis weighed 1 mg or less. A semimicro balance was used for weighing the samples.

RESULTS AND DISCUSSION

Removal of paper matrix by prepyrolysis

Low-temperature pyrolysis (prepyrolysis) conditions were sought which would substantially destroy the paper and leave intact the polymeric additives and coatings. The paper's contribution to a subsequent higher temperature

pyrogram would thus be minimized. Because cellulose has been shown to undergo pyrolysis at 300-500°C [9], prepyrolysis of the pulp samples was studied in that range.

The prepyrolysis temperature was increased in increments above 300°C; 400°C was found to be the lowest temperature at which most of the pulp was charred. At prepyrolysis temperatures above 400°C, significant additional changes in the pulp were not observed. Figure 1 shows pyrograms (850°C) of the bleached hardwood kraft pulp with and without prepyrolysis at 400°C. It is evident that most of the pulp was pyrolyzed at 400°C, leaving little to contribute to the high-temperature pyrogram. Similar results were obtained on the unbleached softwood kraft and the TMP pulps. The area of the major peak in the high-temperature pyrogram of bleached, unbleached, and TMP pulp was reduced by 97, 91, and 80%, respectively, after prepyrolysis.

(Fig. 1 here)

Effect of prepyrolysis on polymers

Twenty-one polymers were subjected to pyrolysis (850°C) and to the prepyrolysis (400°C) - pyrolysis sequence. The area of the major peak in the high-temperature pyrogram of the 12 polymers in Table I was reduced by almost one-half or less as a result of prepyrolysis. Thus, sufficient quantities of these polymers, when added to paper, would be expected to survive the paper's charring in prepyrolysis to be identified by subsequent pyrolysis at higher temperature. An example of the performance of these polymers is shown in Fig. 2; the pyrogram of polyvinyl butyral was virtually unchanged by prepyrolysis. Additional examples of fingerprint pyrograms obtained after prepyrolysis are shown in Fig. 3.

(Table I and Fig. 2 and 3 here)

Because substantial reductions in peak areas were sustained in prepyrolysis, the nine polymers in Table II are less likely to be identifiable in paper by the sequential pyrolysis technique. Despite large peak area reductions, four of the polymers, polyvinyl chloride, methyl and ethyl cellulose, and polyacrylamide, exhibited characteristic high-temperature pyrograms after prepyrolysis. Later work showed, however, that these materials could not be readily determined in paper by PGC.

(Table II here)

Compilation of library of pyrograms

The polymers listed in Table I were found to yield characteristic "fingerprint" pyrograms with well resolved peaks. In uncomplicated samples these materials should be identifiable from their pyrograms by inspection. As a further aid to polymer identification, the pyrolysis products represented by the principal peaks on the pyrograms were identified by PGC/MS. Peak identifications are listed in Table III. These data should faciliate use of PGC/MS to analyze polymer mixtures which yield pyrograms too complex for visual interpretation.

(Table III here)

Identification of polymers in paper

Each of the polymers listed in Table I was added to paper and subjected to sequential pyrolysis. The resulting pyrograms matched the library pyrograms of the polymers, as is illustrated by the example in Fig. 4. Amounts of polymer in the polymer-paper combinations ranged from 18 to 81%; the higher amounts were those polymers added as melts. A high polymer-to-paper ratio would be typical of a deposit or a polymer-paper laminate but not of a pigment-coated paper with a polymer binder.

(Fig. 4 here)

As a final test of the PGC procedure, sequential pyrolysis was used to analyze a commercially-prepared wrapping paper (polyethylene-coated freezer wrap). Pyrograms from the coated paper and the library, shown in Fig. 5, display some differences in peak heights, but the match between the polyethylene in the paper and in the library is quite evident.

(Fig. 5 here)

Results of this study show that prepyrolysis can be used to minimize the contribution of the paper matrix and simplify the identification of many polymers in paper by PGC.

ACKNOWLEDGMENT

Portions of this work were used by TDC as partial fulfillment of the requirements for the Master of Science degree at The Institute of Paper Chemistry.

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TABLE I

EFFECT OF PREPYROLYSIS ON POLYMERS*

Sample	Retention time of major peak (min)	Reduction of peak area (%)
Styrene butadiene	27.84	4
Polybutyl acrylate	13.09	13
Polyethyl acrylate	17.08	53
Polyethylene	15.54	50
Polypropylene	10.10	29
Polyvinyl butyral	10.26	15
Styrene maleic anhydride	27.84	51
Polyamide resin	15.53	4
Acrylonitrile styrene butadiene	28.22	13
Styrene isoprene	27.99	25
Ethylene vinyl acetate	6.46	3
Polystyrene	27.83	10

* The area of the major peak in the high-temperature pyrogram of these polymers was reduced by about one-half or less in prepyrolysis.

TABLE II

EFFECT OF PREPYROLYSIS ON POLYMERS*

Sample	Retention time of major peak (min)	Reduction of peak area (%)
Polyvinyl alcohol	13.18	96
Melamine formaldehyde resin	No characteristic pattern	--
Polyvinyl acetate	12.27	90
Polyvinyl chloride	14.97	88
Polyvinylidene chloride	Very low response	--
Methyl cellulose	9.22	68
Cationic starch	5.95	78
Ethyl cellulose	4.23	61
Polyacrylamide	6.58	72

* These polymers experienced substantial pyrolysis under prepyrolysis conditions.

TABLE III

PYROLYSIS PRODUCTS IDENTIFIED BY PGC/MS

Sample	Retention time of main peak (min)	PGC/MS identification*
Styrene butadiene	6.46	1,3-butadiene
	9.11	1,3-cyclopentadiene
	14.93	benzene
	21.19	toluene
	24.23	ethylbenzene
	27.84	styrene
Polybutyl acrylate	5.53	isobutene
	10.15	butyraldehyde
	13.09	butyl alcohol
	25.92	butyl acrylate
Polyethyl acrylate	4.39	ethanol
	15.79	benzene
	17.08	ethyl acrylate
	21.32	toluene
Polyethylene	5.44	2-methyl propene
	6.61	1,3-butadiene
	9.01	cyclopentene
	9.27	1,3-cyclopentadiene
	10.36	1,1-dimethylcyclopropane
	12.61	1-pentyne
	13.41	1,3-pentadiene
	14.66	cyclohexene
	15.13	benzene
	15.54	1,4-cyclohexadiene
	20.47	1-heptene
	21.44	toluene
Polypropylene	5.28	isobutane
	5.85	isobutene
	6.42	1,2-butadiene
	9.07	1,3-cyclopentadiene
	10.10	1,1-dimethylcyclopropane
	10.89	2-methyl-2-butene
	11.22	N-pentane
	11.44	cyclopentene
	14.81	1-hexene
	15.19	1,4-cyclohexadiene
	16.50	1,4-dimethyl-1,3-pentadiene
	17.83	2,4-dimethyl-1-pentene
	18.19	2-methylfuran
	18.75	2-methyl-1,5-hexadiene
	21.20	toluene
	26.85	2-ethyl-1-butanol

* See end of table for footnotes.

TABLE III (Continued)

PYROLYSIS PRODUCTS IDENTIFIED BY PGC/MS

Sample	Retention time of main peak (min)	PGC/MS identification*
Polyvinyl butyral	5.32	1-butene
	5.81	acetone
	6.48	1,2-butadiene
	9.12	1,3-cyclopentadiene
	10.26	butyraldehyde
	13.16	2-butenal
	14.96	benzene
	21.26	toluene
Styrene maleic anhydride	15.15	benzene
	21.40	toluene
	24.53	ethylbenzene
	28.28	styrene
Polyamide resin	5.43	isobutene
	6.22	propenitrile
	6.59	1,3-butadiene
	9.26	1,3-cyclopentadiene
	10.35	1,1-dimethylcyclopropane
	11.41	isoprene
	15.10	benzene
	15.53	1-hexane
	16.62	N-hexane
	20.45	1-heptene
	21.40	toluene
	25.27	1-octene
Acrylonitrile styrene butadiene	6.66	1,3-butadiene
	15.15	benzene
	21.43	toluene
	24.52	ethylbenzene
	28.22	styrene
Styrene isoprene	5.85	isobutene
	6.52	1,2-butadiene
	11.60	isoprene
	15.02	benzene
	15.27	cyclohexadiene
	21.27	toluene
	24.36	ethylbenzene
	27.99	styrene
	29.44	xylene

* See end of table for footnotes.

TABLE III (Continued)

PYROLYSIS PRODUCTS IDENTIFIED BY PGC/MS

Sample	Retention time of main peak (min)	PGC/MS identification*
Ethylene vinyl acetate	5.32	2-butene
	6.46	1,2-butadiene
	9.12	1,3-cyclopentadiene
	10.21	ethylcyclopropane
	11.14	acetic acid
	13.21	cyclopentene
	14.93	benzene
	15.36	1-hexene
	20.28	1-heptene
	21.22	toluene
Polystyrene	14.98	benzene
	21.17	toluene
	24.18	ethylbenzene
	27.83	styrene

*Identifications are based on the best match of an unknown spectrum with spectra in the Wiley Library.

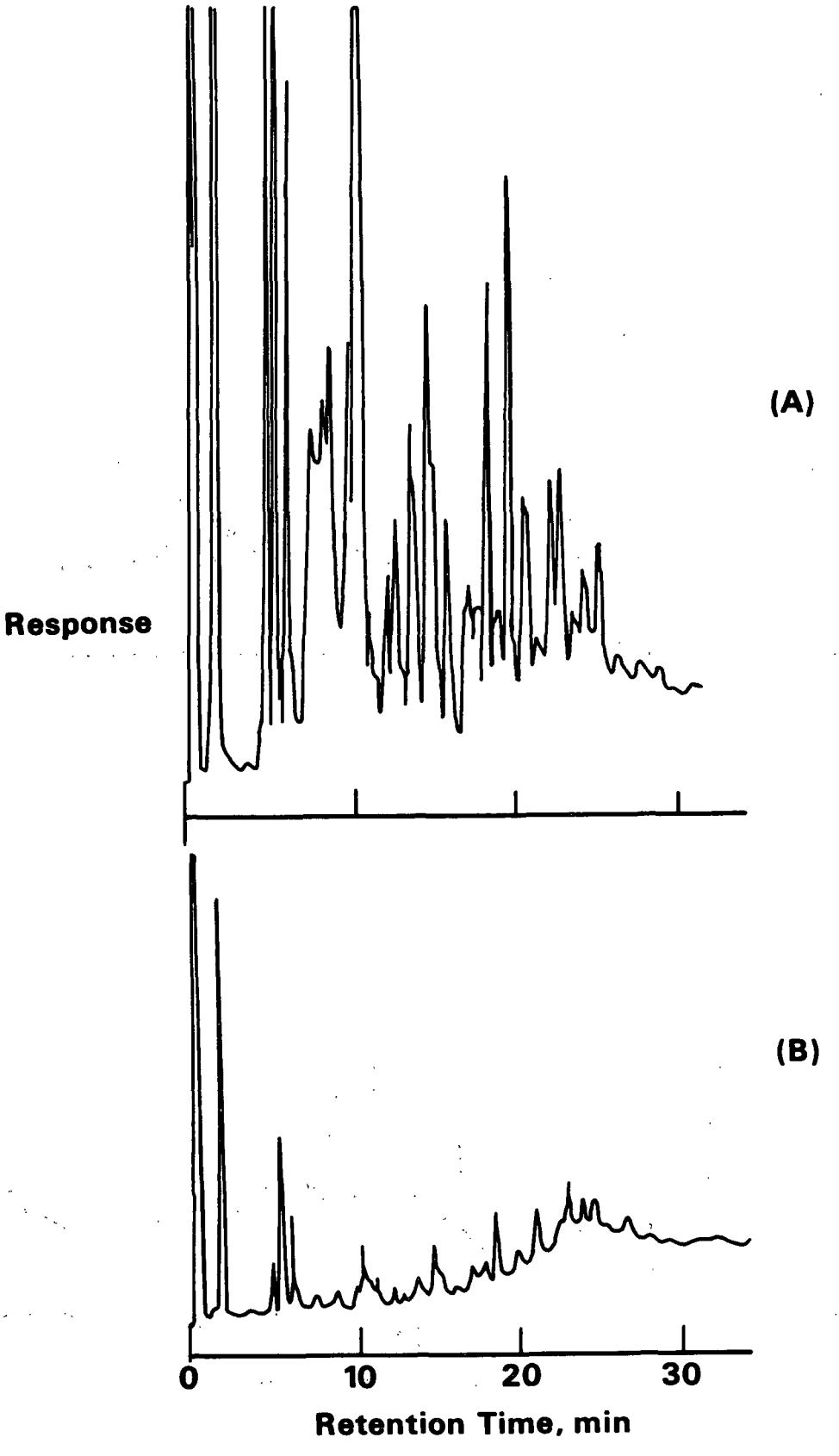

Fig. 1. Pyrogram of (A) bleached hardwood kraft pulp and (B) same after prepyrolysis.

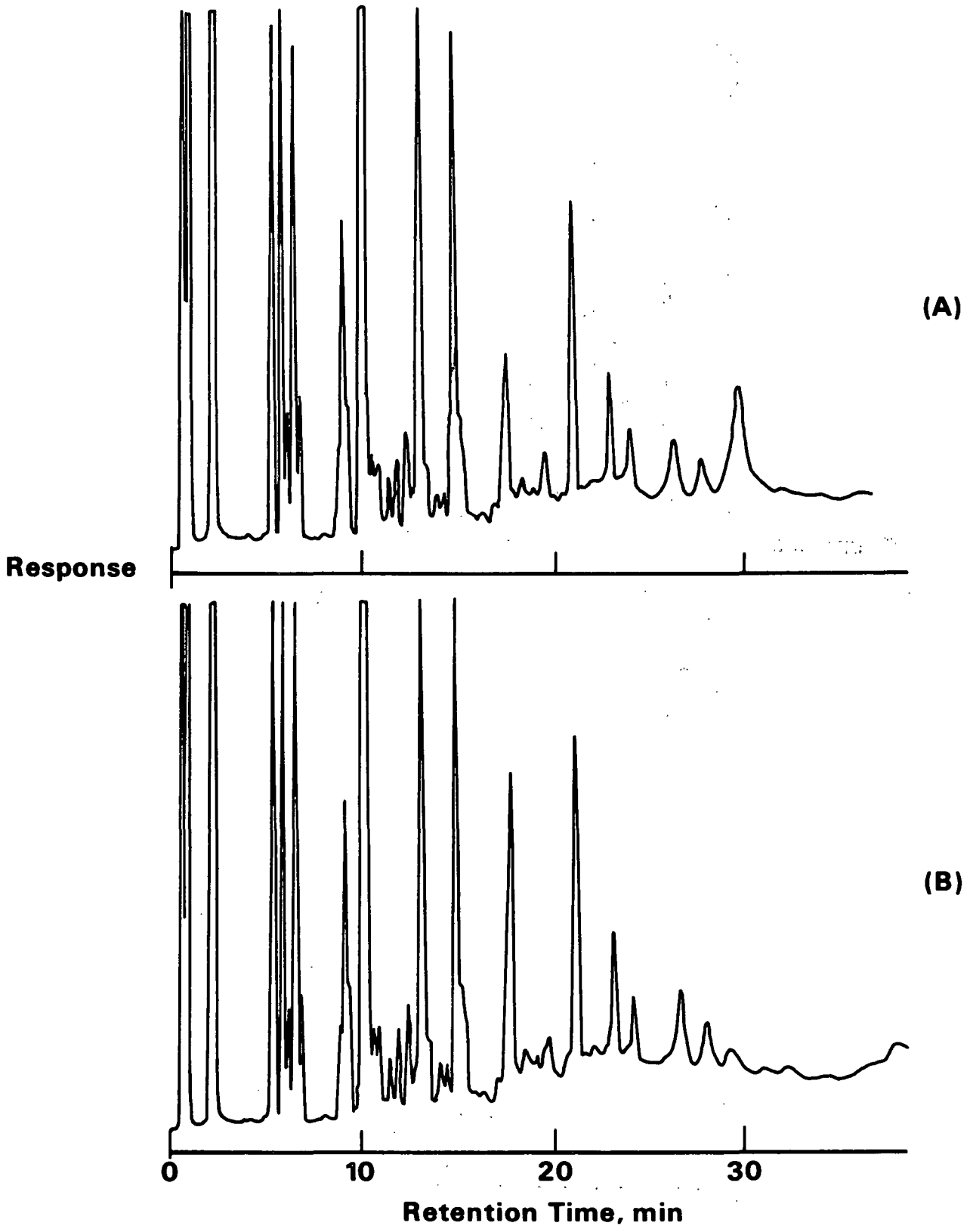

Fig. 2. Pyrogram of (A) polyvinyl butyral and (B) same after prepyrolysis.

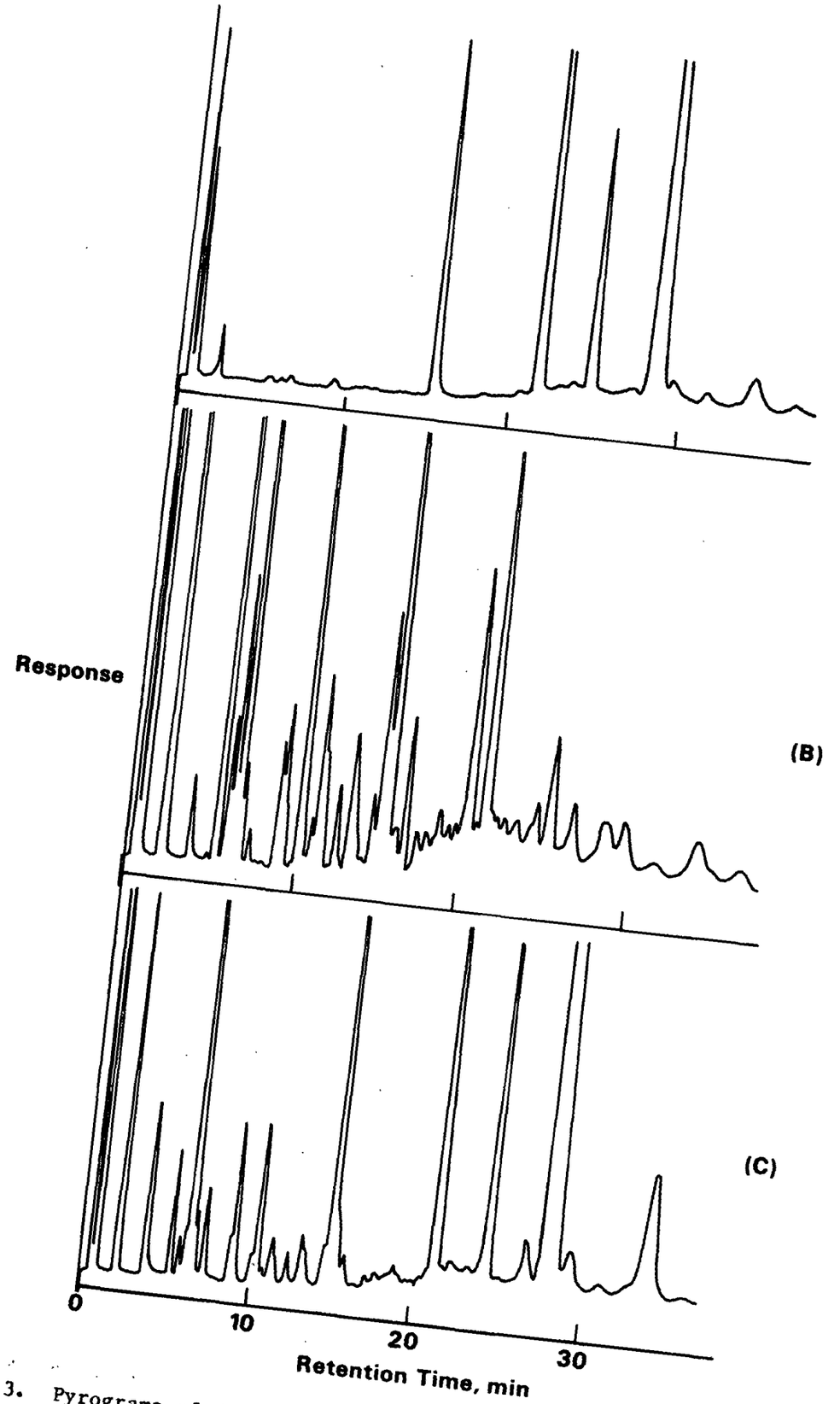

Fig. 3. Pyrograms of (A) styrene maleic anhydride, (B) polyamide resin, and (C) acrylonitrile styrene butadiene, all after prepyrolysis.

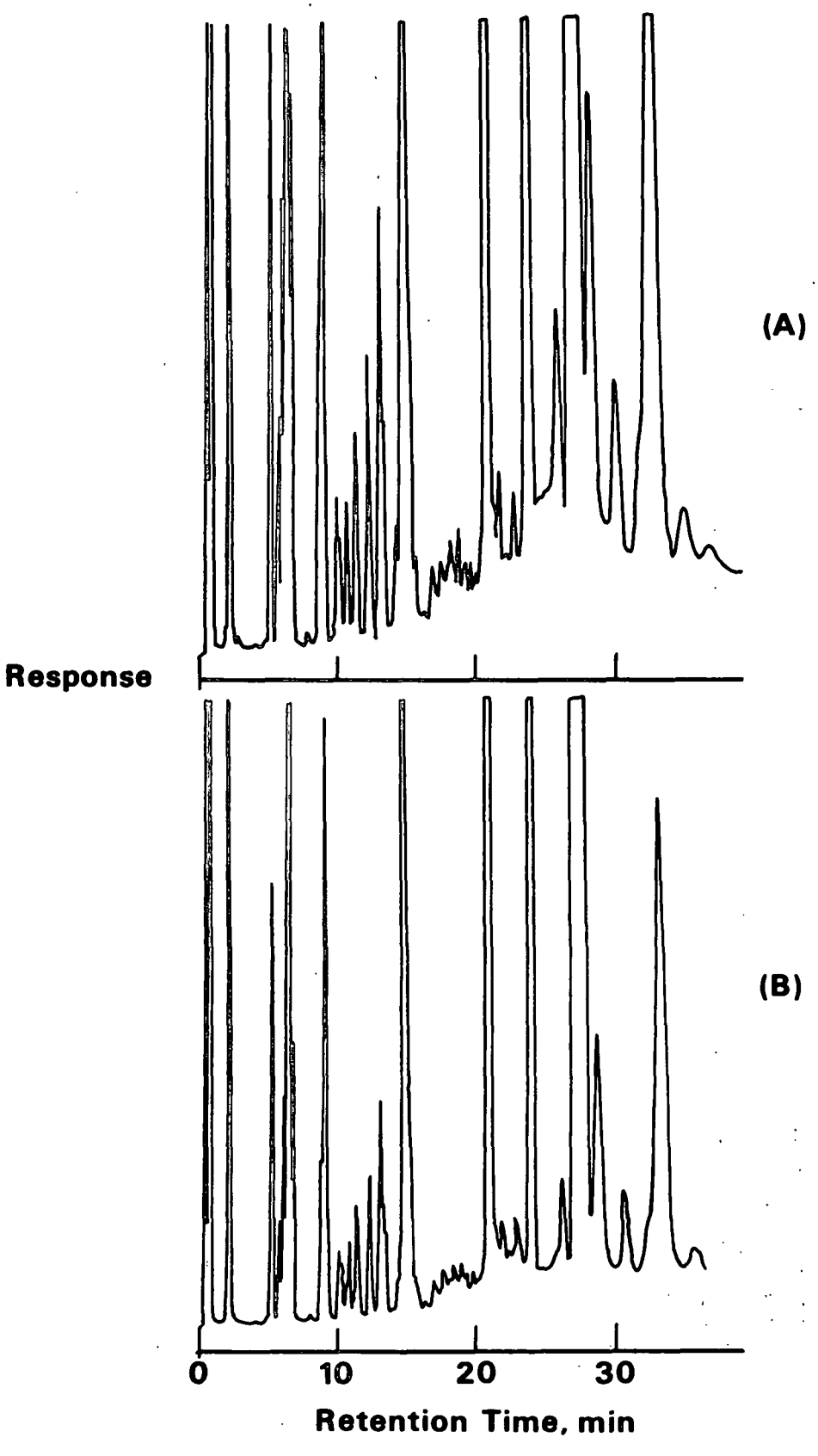

Fig. 4. Pyrogram of (A) styrene butadiene alone and (B) after addition to paper, both after prepyrolysis.

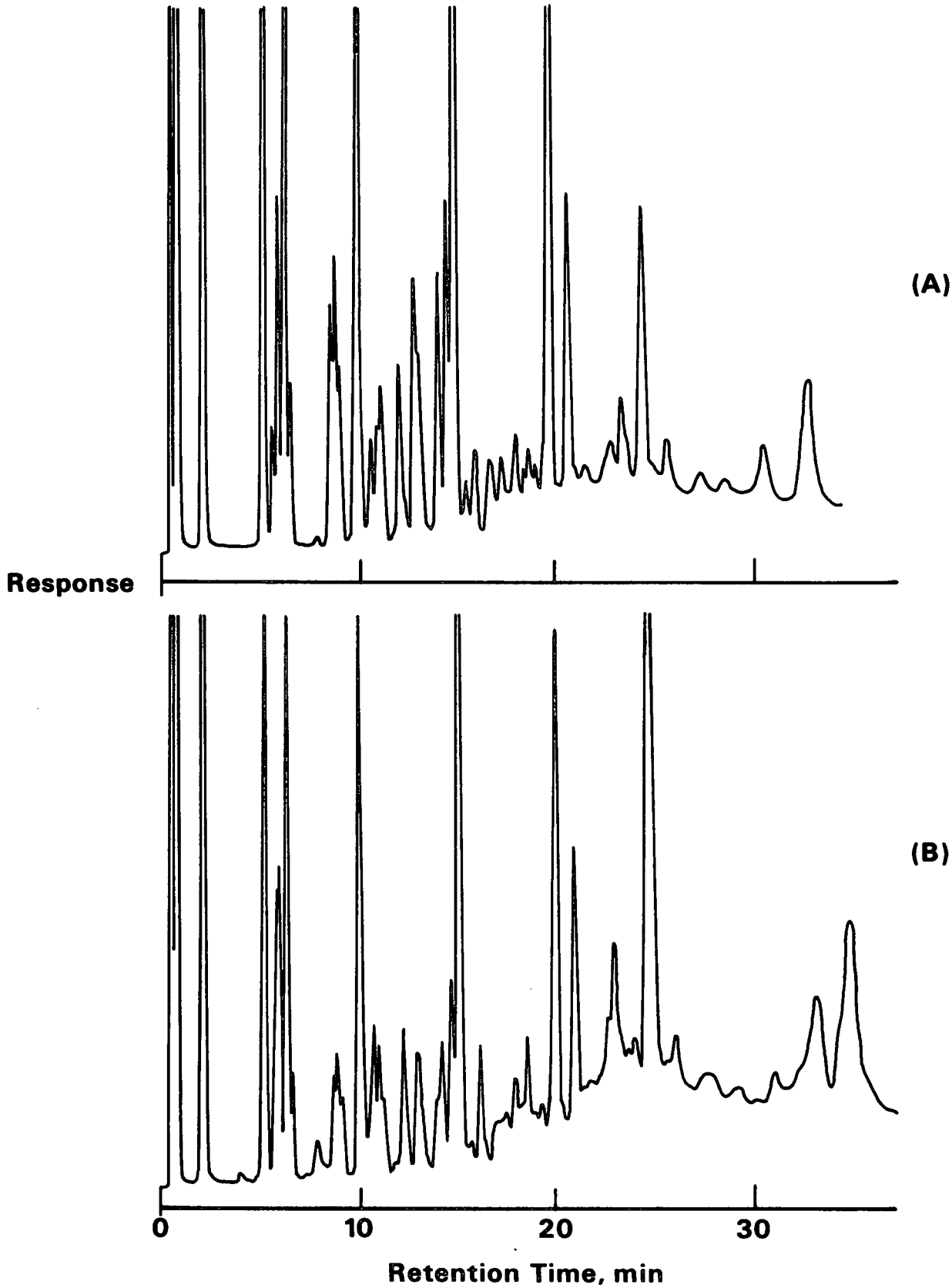

Fig. 5. Pyrogram of polyethylene (A) from library and (B) in commercially prepared freezer wrap paper, both after prepyrolysis.